Metastable high-pressure single-bonded phases of nitrogen predicted via genetic algorithm

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The recently proposed genetic algorithm for crystal structure prediction combined with first-principles structural optimizations is used to investigate the high-pressure structures of solid nitrogen. Starting from a population of randomly generated eight-atom structures at 80 GPa, the evolutionary process not only recovers the four lowest-energy nonmolecular structures (CG, $C2/c$, black phosphorus, and *Cmcm* chain) predicted theoretically or known experimentally, but also reveals a metastable single-bonded three-dimensional structure. The stability of this structure at 80 GPa is established by phonon calculations. At this pressure, the enthalpy of the structure is 0.17 eV/atom higher than that of the *cubic gauche* phase. The energetic difference between this structure and other nonmolecular high-pressure phases is explained from analysis of the local structural motifs.

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At ambient pressure nitrogen forms diatomic molecules with triple covalent bonds. Under high pressure, the molecular structure undergoes phase transitions into nonmolecular structures. Since the dissociation energy of a triple bond is extremely high, the decomposition of a nonmolecular structure back into the molecular form, if could be realized, would release a large amount of energy. Therefore, nonmolecular nitrogen compounds might serve as potential high-energy storage materials and have been investigated for decades.

Single-bonded (SB) group-V elemental structures tend to derive from the simple cubic (sc) structure. Therefore many theoretical predictions of nonmolecular nitrogen started from distortion of the sc structure.[1] For example, the earlier proposed *A*7 and black phosphorus (BP) structures were obtained from rhombohedral and orthorhombic distortions of the sc structure, respectively.[1] Recently a systematic search method spanning all possible distortions of the sc structure was developed and several new SB structures were proposed.[2] The other group of nonmolecular nitrogen has a chainlike structure in which nitrogen atoms are connected by alternating single and double bonds—e.g., the *Cmcm* (Ref. 3) and *Imma* (Ref. 4) chain structures. A breakthrough in investigating nonmolecular nitrogen is the theoretical prediction[1] of the *cubic gauche* (CG) structure. The CG structure is formed solely from single bonds and predicted to have the lowest energy at high pressure. After intensive efforts, the CG structure was successfully synthesized in the laboratory.[5] Recently, new structural prediction techniques have revealed several new structures.[2,6–8] In the present study, the recently proposed genetic algorithm[7,9–12] (GA) is used to search for high-pressure nonmolecular SB structures of nitrogen. We not only recover the lowest-energy structures[1,3,7] (CG, $C2/c$, BP, and *Cmcm* chain), but also reveal a metastable SB structure.

The application of the GA[13,14] in structural predictions can be traced back to the determination of the structures of carbon fullerene clusters.[15] An earlier approach encoding structural information with binary strings has gained considerable successes, but it is not very efficient for complicated systems.[16–18] Recently a new approach has been proposed[7] for crystal structure predictions that requires no prior knowledge of structural information except for the numbers of the constituent elements in the unit cell.[7,9–12] The search starts with a population of randomly generated structures. The population is improved through genetic operations by producing energetically favorable structures. In successive generations, new low-energy structures evolve and replace the highest-energy structures in the preceding generation. In this paper, results on the application of this approach to investigate nonmolecular SB nitrogen structures at high pressure are reported.

A computer code has been developed that comprises several recently proposed strategies[7,9–12] with additional features that were found to make the GA search more efficient in our case. In this method, low-energy candidate structures are generated in successive cycles of heredity and mutation operations followed by structural optimizations.[7,9–12] To evolve an offspring structure from two parent structures, the heredity operation of "cutting, shifting and splicing"[15] adapted to periodic systems[7,9–12] was used. Mutation operation applies distortions on unit cells and/or atomic positions of a parent structure to generate offspring.[7,11,12] A retaining operation was applied on the population after structural optimizations. The procedure kept a small subset of lowest-energy structures in the population to pass their genomes onto successive generations. It is noteworthy that the GA tends to produce a large number of identical low-energy structures. An ideal scenario is that during the evolution, the lowest-energy (fittest) structure evolves, reproduces itself, and eventually dominates the entire population. The considerable redundancy constitutes a statistically strong indication that the redundant structures are energetically favored.[19,20] However, under high pressure, it is not uncommon that metastable structures with slightly higher energies can exist. In this aspect, to avoid eliminating metastable structures, it is helpful to remove the redundancy of the lowest-energy structures and retain only a single copy from the set of identical low-energy structures in the population. The preference for the fittest structure is then decided by the fitness rank,[7,9–12] i.e., the lower-energy structure has higher priority, being selected as a parent structure. A structure analysis package has been implemented to examine structural similarity based on comparison of the radial distribution functions (RDFs) and space-group symmetries[21] of the fully relaxed structures. Distinguishing structurally distinct structures, besides being

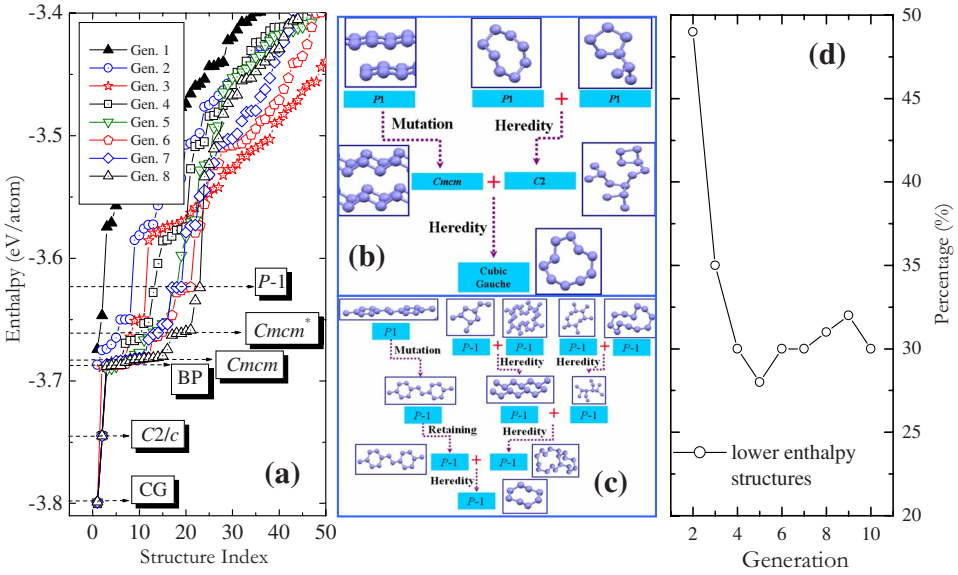


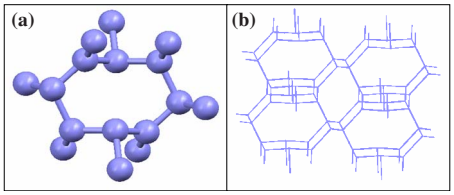
FIG. 1. (Color online) (a) The evolutionary procedure showing the first eight generations by different symbol curves. The resulting structures are sorted in order of increasing enthalpy. The *Cmcm* structure marked with the asterisk is a distorted form of the known *Cmcm* chain structure (Ref. 3). (b) The detailed evolution of the CG structure recovered in the third generation. (c) The detailed evolution of the new $P\bar{1}$ structure found in the fourth generation. (d) The searching efficiency analysis for the first ten generations; the percentage of offspring structures having lower enthalpies than their parents as a function of generation.

used in the "retaining" operation, is useful for the heredity operations to avoid mating between *identical* structures. A monitoring routine has been developed to trace the evolutionary history and analyze the production efficiency. Specifically, for each generation, a record of (i) the number of offspring structures having lower energy than their parents, (ii) the number of offspring structures different from their parents, and (iii) structural information and space groups of newly generated and disappeared structures is kept. These records are needed for analysis of the evolutionary track of new structures from the closest kin. An example of this analysis is presented in Fig. 1 and will be discussed in detail below.

The search for high-pressure structures of nitrogen at 80 GPa has been performed with a population of 80 eight-atom unit cells. The eight-atom model represents possible structures with one, two, four, and eight atoms per primitive cell. Hard constraints are applied on the minimum allowed N-N distance, cell angles, and lengths of cell vectors of the generated structures.[7,11,12] In each generation, the top 20% highest-enthalpy structures are rejected. In the generation of new offspring structures, the parents are chosen according to the enthalpies (fitness score). Ten percent of the structures in the new generation are retained from the previous generation. Seventy percent of the structures are produced from heredity operations and the remaining 20% from mutation operations. The atomic volume, unit cell shape, and atomic positions of each candidate structure are fully optimized at constant pressure.[22,23] Electronic calculations are performed with the VASP code[24] employing a projected-augmented-wave (PAW) pseudopotential[25] and a plane-wave energy cutoff of 910 eV. The generalized-gradient approximation[26] (GGA, Perdew-Burke-Ernzerhof) exchange-correlation functional is employed. No symmetry is assumed in the calculations. The *k*-point grids[27] are generated by scaling according to the length of the reciprocal lattice vectors of the structure[11] with a basic division of 4 and rounded to the nearest higher even integers. The lowest-enthalpy structures evolved from each generation are reoptimized with more stringent convergence criteria and by doubling the size of the *k*-point grid.

The evolution cycle is repeated until no new low-enthalpy structures are generated in several successive generations. By using the retaining operation, best-fit structures in each generation are carried over to the next generation. A criterion for convergence of the evolution is that the subset of the lowest-enthalpy structures and their relative energy order be maintained within several new generations. In the present study the evolution is performed for 20 generations. Figure 1(a) shows the results of the first eight generations. The structures are sorted in order of increasing enthalpy, and thus the first structure in each generation is the lowest-enthalpy structure. The efficiency of the evolution is analyzed and summarized in Fig. 1(d). The structures of the first ten generations are compared with their parents from previous generations. The percentage of offsprings having lower enthalpies than their parents is indicated by open circles [Fig. 1(d)]. The percentage was initially fairly high but decreased dramatically and then stabilized around 30%. This observation reveals the evolutionary trend of "chaos" → "local minima" → "neighborhood spanning" on the free-energy surface. As shown in Fig. 1(a) the first known nonmolecular structure that appears is the *Cmcm* chain structure[3] which has the lowest enthalpy in the second generation. The CG structure appears in the third generation. The evolution of the CG structure is presented in Fig. 1(b). The structure is the heredity offspring of the *Cmcm* chain structure and a higher-enthalpy SB *C*2 structure. The *Cmcm* chain and *C*2 structures are both offspring of distinct *P*1 structures. The discovery of the CG structure from the GA is not trivial. The CG structure exhibits all-*gauche* helicity in which all dihedral angles in single bonds have the *gauche* conformation to minimize the internal energy.[1] This unique structural topology makes it isolated in energy space by high activation barriers. The present result highlights the efficiency of the GA in sampling of the free-energy surface. It is noteworthy that the efficiency of the GA, at least for this particular case, seems to be superior over the random-search method.[28] The random-search

TABLE I. (Color online) Details of the new $P\bar{1}$ structure at 80 GPa. (a) The primitive cell shows a puckered eight-member ring. (b) Connections between the eight-member rings in the crystal structure.



Pressure (GPa)	Space group	Lattice parameters (Å, deg)	Atomic coordinates (fractional)
80	$P\bar{1}$	a=3.13 b=3.48 c=4.51	2*i* 0.8226 0.1801 0.5103
		α=71.22 β=83.18 γ=74.41	2*i* 0.8528 0.4956 0.2508
			2*i* 0.4838 0.3398 0.9432
			2*i* 0.8892 0.2526 0.7701

method was attempted by us but failed to obtain the correct CG structure from over 500 trial structures. In comparison, the GA successfully locates the CG structure in the third generation with only 240 candidate structures.

A SB structure with $P\bar{1}$ symmetry appears in the fourth generation. Figure 1(c) shows its evolutionary pathway. This structure has eight atoms in the primitive cell, and the structural details at 80 GPa are given in Table I. Inset (a) of Table I shows that the eight nitrogen atoms are arranged in a puckered eight-member ring with inversion symmetry. Each ring is connected to six neighboring rings with alternating *gauche*- and *trans*-dihedral angles. This topology is energetically favorable since the *gauche*- and *trans*-dihedral angles are two minimum-energy conformers[1,29] in SB nitrogen (see below).

The equation of states of the new $P\bar{1}$ structure and several earlier proposed structures are compared in Fig. 2. At 80 GPa, the new $P\bar{1}$ structure is the fifth lowest-enthalpy phase, ca. 0.17 eV/atom higher than the CG phase. The enthalpy of the $P\bar{1}$ structure approaches that of the *Cmcm* chain structure with increasing pressure and becomes lower at ca. 110 GPa. Besides the CG and *Cmcm* chain structures, two lowest-enthalpy structures proposed earlier, the $C2/c$ (Ref. 7) and BP (Ref. 1) structures, are recovered in the fourth and sixth generations, respectively [Fig. 1(a)]. However, the *A*7,[1] No. 8,[2] No. 11,[2] and *Imma* chain[4] (not shown) structures were not observed. These structures have higher enthalpies than that of the new $P\bar{1}$ structure, with the enthalpy difference varying from 0.08 to 0.45 eV/atom at 80 GPa. Since the GA is based on "survival of the fittest," only a subset of the lowest-enthalpy structures survives. Structures with too high enthalpy are simply annihilated and do not evolve further. Besides the structures discussed above, there are two other proposed SB nitrogen structures, LB (Ref. 6) and CW

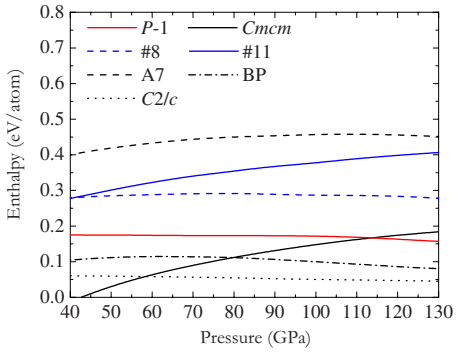


FIG. 2. (Color online) Enthalpies per nitrogen atom of the new $P\bar{1}$ structure and selected earlier proposed nonmolecular structures as functions of pressure. The enthalpy of the CG structure is taken as reference.

(Ref. 8). The LB structure has been proven to be unstable via phonon calculations.[2] The CW structure has six atoms per primitive cell and therefore not obtained in the present eight-atom simulation. However, using the reported structure,[8] the enthalpy is found to be 0.03 eV/atom higher than that of the new $P\bar{1}$ structure at 80 GPa.

The energetic order of the lowest-energy SB structures shown in Fig. 2 can be understood from the analysis of the long-pair interaction between adjacent nitrogen atoms. Theoretical investigations[29–31] on X_2N-NX_2 (X=F,H, etc.) isomers have shown that the interaction is characterized by the dihedral angle. The most unstable structure is the *cis* conformation with the zero dihedral angle. As the dihedral angle increases, the bond energy decreases and reaches a minimum at the *gauche* conformation. For example, in the CG struc-

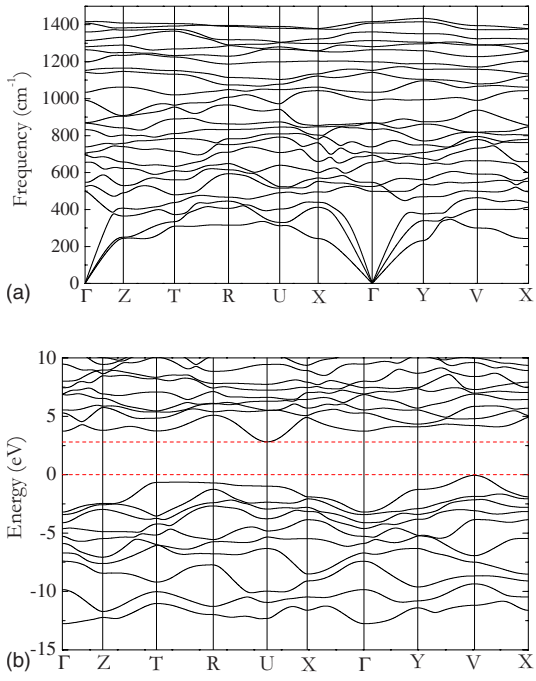


FIG. 3. (Color online) The phonon dispersion (a) and electronic band structure (b) of the new $P\bar{1}$ structure calculated at 80 GPa.

ture the *gauche* angle is 107°.[1] The second energy minimum is found at the *trans* conformation with the dihedral angle of 180°. In the CG structure, nitrogen atoms are arranged entirely in the *gauche* conformation and therefore have the lowest enthalpy. The BP structure, having both *gauche*- and *trans*-dihedral angles, is the second-lowest-energy structure and has only 0.11 eV/atom higher energy than that of the CG structure at 80 GPa. In the new $P\bar{1}$ structure, four out of the eight dihedral angles ($\pm 125°, \pm 106°$) in the eight-member ring are close to the global minimum identified by the *gauche* arrangement. The remaining four dihedral angles of $\pm 48°$ and $\pm 27°$, especially the latter, are close to the *cis* conformation, and therefore the energy is higher than that of both the CG and BP structures.

To examine the stability of the new $P\bar{1}$ structure the phonon dispersion has been calculated at 80 GPa. The results are presented in Fig. 3(a). The absence of imaginary frequency mode confirms that the new $P\bar{1}$ structure is stable. The electronic band structure at 80 GPa [Fig. 3(b)] shows that this structure is an insulator with an indirect band gap of 2.8 eV between the *U* and *V* points. The electronic and phonon calculations were performed within the density-functional perturbation theory[32,33] using the QUANTUM-ESPRESSO package.[34] A carefully calibrated Vanderbilt ultrasoft potential[35] with generalized-gradient approximation[26] was used. The electronic band structure was calculated with a $16\times16\times12$ Monkhorst-Pack[27] (MP) *k*-point mesh for the first Brillouin zone (BZ) sampling. Phonon calculations were performed with a $4\times4\times3$ MP phonon *q*-point mesh and an $8\times8\times6$ MP electronic *k*-point mesh for the first BZ sampling.

In conclusion, the recently proposed genetic algorithm for crystal structure prediction with first-principles structural optimizations has been applied to investigate SB structures of nitrogen at 80 GPa. The four observed or predicted lowest-energy structures CG, $C2/c$, BP, and *Cmcm* chain have been identified successfully. A SB nitrogen structure with three-dimensionally connected eight-member rings has been discovered. This structure is stable and has only 0.17 eV/atom higher enthalpy than that of the CG phase at 80 GPa. The energy difference between this structure and other (meta) stable SB structures is rationalized from their local structural motifs. This structure was not observed in a previously proposed search procedure[2] based on rearrangements and distortions of simple cubic cells.

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[1] C. Mailhiot, L. H. Yang, and A. K. McMahan, Phys. Rev. B **46**, 14419 (1992).
[2] F. Zahariev, S. V. Dudiy, J. Hooper, F. Zhang, and T. K. Woo, Phys. Rev. Lett. **97**, 155503 (2006).
[3] W. D. Mattson, D. Sanchez-Portal, S. Chiesa, and R. M. Martin, Phys. Rev. Lett. **93**, 125501 (2004).
[4] M. M. G. Alemany and J. L. Martins, Phys. Rev. B **68**, 024110 (2003).
[5] M. I. Eremets, A. G. Gavriliuk, I. A. Trojan, D. A. Dzivenko, and R. Boehler, Nat. Mater. **3**, 558 (2004).
[6] F. Zahariev, A. Hu, J. Hooper, F. Zhang, and T. K. Woo, Phys. Rev. B **72**, 214108 (2005).
[7] A. R. Oganov and C. W. Glass, J. Chem. Phys. **124**, 244704 (2006).
[8] F. Zahariev, J. Hooper, S. Alavi, F. Zhang, and T. K. Woo, Phys. Rev. B **75**, 140101(R) (2007).
[9] N. L. Abraham and M. I. J. Probert, Phys. Rev. B **73**, 224104 (2006).
[10] A. R. Oganov, C. W. Glass, and S. Ono, Earth Planet. Sci. Lett. **241**, 95 (2006).
[11] C. W. Glass, A. R. Oganov, and N. Hansen, Comput. Phys. Commun. **175**, 713 (2006).
[12] G. Trimarchi and A. Zunger, Phys. Rev. B **75**, 104113 (2007).
[13] Z. Michalewicz and D. B. Fogel, *How to Solve It: Modern Heuristics* (Springer, Berlin, 2000).
[14] A. E. Eiben and J. E. Smith, *Introduction to Evolutionary Computing* (Springer, Berlin, 2003).
[15] D. M. Deaven and K. M. Ho, Phys. Rev. Lett. **75**, 288 (1995).
[16] T. S. Bush, C. R. A. Catlow, and P. D. Battle, J. Mater. Chem. **5**, 1269 (1995).
[17] S. M. Woodley, P. D. Battle, J. D. Gale, and C. R. A. Catlow, Phys. Chem. Chem. Phys. **1**, 2535 (1999).
[18] S. M. Woodley, Struct. Bonding (Berlin) **110**, 95 (2004).
[19] S. V. Barabash, V. Blum, S. Müller, and A. Zunger, Phys. Rev. B **74**, 035108 (2006).
[20] G. L. W. Hart, V. Blum, M. J. Walorski, and A. Zunger, Nat. Mater. **4**, 391 (2005).
[21] H. T. Stokes, D. M. Hatch, and B. J. Campbell, http://stokes.byu.edu/isotropy.html
[22] O. H. Nielsen and R. M. Martin, Phys. Rev. B **32**, 3780 (1985).
[23] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).
[24] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
[25] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[26] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[27] H. J. Monkhorst and J. D. Park, Phys. Rev. B **13**, 5188 (1976).
[28] C. J. Pickard and R. J. Needs, Phys. Rev. Lett. **97**, 045504 (2006).
[29] L. Radom, J. Baker, P. M. W. Gill, R. H. Nobes, and N. V. Riggs, J. Mol. Struct.: THEOCHEM **126**, 271 (1985).
[30] A. H. Cowley, D. J. Mitchell, M. H. Whangbo, and S. Wolfe, J. Am. Chem. Soc. **101**, 5224 (1979).
[31] J. O. Williams, J. N. Scarsdale, L. Schäfer, and H. J. Geise, J. Mol. Struct.: THEOCHEM **76**, 11 (1981).
[32] S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987).
[33] P. Giannozzi, S. de Gironcoli, P. Pavone, and S. Baroni, Phys. Rev. B **43**, 7231 (1991).
[34] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001); http://www.pwscf.org
[35] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).